WEAK QUANTIZATION

By Paul Ehrenfest and Richard C. Tolman

Abstract

Quantization is called weak when a motion apparently allowed by the equation $\int pdq=nh$, has less than the normal a-priori weight. It is believed that the deficiency in a-priori weight is taken over, either by neighboring classically allowed motions, or by neighboring strongly quantized motions when such are present in the region of the phase-space considered. Weak quantization is to be expected when uncertainties arise as to the period that should be used in determining the limits of the phase integral $\int pdq$. Several cases are considered; (a) when the period is so long that there is considerable chance of interruption by a quantum transition; (b) when a system has two apparent periods, a long true period T and a short quasi-period θ; (c) when the periodicity is disturbed frequently in a fortuitous manner as by molecular collisions. In case (b), the tendency towards quantization with respect to T may be gradually replaced by quantization with respect to θ as T is lengthened, and then the probability of quantum transitions which correspond to quantization with respect to T is weakened while that of transitions related to θ is strengthened. This suggests the possibility that the strengthening of the probability of transitions related to a period θ may be accompanied by a strengthening of quantization with respect to that period.

BOHR has called attention to the dangers of applying the simple rules of quantization in too naive a fashion, since there may be cases in which there is merely a tendency for the system to assume a particular motion apparently allowed by the quantum rules. It is the purpose of the following article to consider in a very tentative way a number of different conditions under which we may expect that a motion which is apparently allowed by the simple rules of quantization will not have the full normal probability of existence, and what results may be expected to come from such a "weakening" of the quantization. We desire to make no claim of originality for all of the considerations, but feel that their speculative interest justifies their collection in a single place. Some of the considerations may have a possible bearing on questions of specific heat, the occurrence of the symmetry factor in the chemical constant, the width of spectral lines and other matters of immediate concern.

For simplicity of treatment we shall restrict our primary considerations to systems having a single degree of freedom, and since we shall wish to use the Bohr correspondence principle in the classification and discussion of cases of weak quantization, we shall write the components of the electric moment of the system under consideration as given by Fourier series of the form

$$\xi = \Sigma_\tau C_\tau \ (2\pi\tau\omega t + \gamma_\tau) \tag{1}$$

where τ can assume all integral values, C_τ is the amplitude of the harmonic for a given value of τ, ω is the frequency of the fundamental, and γ_τ is a phase angle.

We may define weak quantization with the help of the idea of the a-priori probability of the different states of motion under consideration. In the classical mechanics, the a-priori probability was considered as spread uniformly over the whole qp phase-space used in describing the motion of the system in question. In the quantum theory the a-priori probability has usually been considered as concentrated and belonging solely to the quantized motions, each motion allowed by the quantum condition

$$\int p dq = nh \tag{2}$$

receiving the a-priori weight h. We shall call the quantization ***weak*** in cases where a motion allowed by Eq. (2) has an a-priori weight less than the normal value h, and the quantization *strong* when the quantized motion has the full normal a-priori probability.

Since it is usually, if not always, possible to arrive at a given condition of weak quantization by an adiabatic transformation from a suitably chosen condition of strong quantization, we shall feel inclined to expect that the decrease below the normal value in the a-priori probability of a weakly quantized motion is taken over by other motions of the system. We may distinguish two cases, those in which the a-priori probability lost by the strictly quantized motion is taken over by the neighboring non-quantized but classically allowed motions, and those in which the a-priori probability is taken over by neighboring strictly quantized motions. We shall find examples of both kinds.

We may now proceed to consider cases of weak quantization, classifying and discussing them with the help of statements as to the magnitudes of the quantities ω and C_τ occurring in Eq. (1).

Case I (Radio oscillator). The period $T = 1/\omega$ is long and one or more values of C_τ are large, for all motions in the region of the phase-space under consideration.

Our present simple rules of quantization, for example in the Wilson-Sommerfeld form given by Eq. (2), are obviously devised solely for application to periodic motions, since the limits of the integration are determined by the period. It is evident, however, that even quantized motions are not rigorously periodic since they are interrupted by sudden transitions to other quantum states. Nevertheless if these interruptions occur only infrequently, we shall have no hesitation in applying the simple rules of quantization by treating the motions as though they were strictly periodic. On the other hand, we should not expect to find strong quantization if the frequency of such transitions should become large enough to be of the same order of magnitude as the frequency of the motion itself. In accordance with the correspondence principle, however, the probability of a given transition in which the quantum number changes by τ will be large when the corresponding Fourier coefficient C_τ is large, hence we shall expect weak quantization for motions with large values of C_τ and small values of ω, or somewhat generally for motions of large amplitude and low frequency. Moreover, we shall expect the tendency towards weak quantization to increase with the ratio $\phi(C_\tau)/\omega$, where $\phi(C_\tau)$ may be roughly regarded as symbolizing the frequency of transition and ω is the frequency of the motion.

In the cases now under consideration, the ratio $\phi(C_\tau)/\omega$ is taken as large for all motions in the general region of the phase-space under consideration. Hence there are no strongly quantized motions in this region of the phase-space, and the defect in a-priori probability below the normal value for strictly quantized motions may be regarded as taken over by classically allowed motions in the same general neighborhood.

It should be noted that in extreme cases where $\phi(C_\tau)/\omega$ becomes very large, our considerations lead to a *complete* replacement of the quantum theory treatment of the phenomenon in question by the classical treatment. For example in the clase of slow oscillations of radio frequency in a Hertzian oscillator, it would seem to be in the spirit of Bohr's thought to say, not merely that the classical picture of the phenomenon *may* be used for purposes of computation because the quanta $h\nu$ have become too small to be appreciable, but rather to say that the classical picture actually *ought* to be used because the motion is really not quantized at all.

An interesting possibility arises in connection with the specific heat of systems of molecules, since both for oscillation and rotation we shall expect the ratio $\phi(C_\tau)/\omega$ to be greater for higher quantum states than for lower states, and hence the quantization to be weakened in the higher states. This will make the specific heat of such systems approach the classical value with rising temperature quicker than is predicted by the usual quantum theory treatments. It seems probable that deviations actually arising from this source would usually be extremely small.

Case II (Alternating rotator). The true period $T=1/\omega$ is long, but the motion has a short quasi-period $\theta=T/F$. C_τ is large only when $\tau=iF(i=1, 2, 3 \ldots .)$.

We shall now consider systems of one degree of freedom in which there is a competition for quantization between two periods, a long true period T after which the system again traces out exactly the same set of motions, and a short quasi-period θ, after which the system has completely returned to its earlier state, with the single exception that it is nearer to the end of the long period T.

To fix our attention, we may use as a simple example[1] of such systems an alternating rotator, which consists of a rigid electric dipole turning about its axis in a field free from force. The period of the rotation is θ, but a kinematic arrangement is provided so that at intervals of period $T=F\theta$ (where F is a large number), the direction of rotation is abruptly reversed by an elastic collision. The quantization of such a motion with the help of Eq. (2) leads to the following paradox. If we use the short quasi-period θ for determining the limits of the phase integral $\int pdq$, we obtain permitted values of the angular momentum which lie far apart, while if we use the longer period T the permitted values of the angular momentum lie very near together. Since the two methods of quantization do not lead to the same result, we must make a choice as to which period to use and should feel obliged to quantize using T since it is the *true* period. If now, however, we make T longer and longer, by changing the setting of the reversing mechanism so as to increase the number F of short periods contained in the true period, the values of the angular momentum allowed by our selected method of quantization get nearer and nearer together, and yet at the limit $F=\infty$ we feel certain that the values which lie far apart as allowed by the other method of quantization are the correct ones.

To elucidate this paradox,[1] one can call attention to the fact that, even though we take T as the correct period of quantization, a Fourier analysis of the motion will lead to values of C_τ which are extremely small unless $\tau \cong F$, and thus the only quantum jumps of any importance will be those in which the angular momentum changes by an amount which would be allowed if we took θ as the correct period for quantization. Hence, even if we quantize using T as the correct period, it is evident that a system of such rotators started in the state of zero rotation and allowed to interact with thermal radiation, would be found distributed, after a *time which is long but not too long*, in the same way as would be predicted on the assumption that θ is the correct period for quantization.

This treatment of the paradox is evidently only partially satisfactory. It makes the arrival of the state of quantization which we feel sure to be

[1] Ehrenfest and Breit, Zeits. f. Phys. 9, 207 (1922)

the correct one dependent on the starting of the rotators in a particular way and it leads to the disappearance of this state of quantization in time provided only one waits long enough.

In consonance with the spirit of our present considerations,[2] a further contribution to the resolution of the paradox is possible. As already pointed out, the quantum conditions, given by Eq. (2), are devised for application to rigorously periodic motions, and yet are actually applied to motions which are periodic only for a time and are then interrupted by quantum transitions. This has already led us in the previous section to the conclusion that we can not usually expect strong quantization for motions of very long periods, since such motions would too often be interrupted by the transitions. We now call attention to the following additional conclusion. Since the quantum conditions are in any case applied to motions which are not rigorously periodic, being interrupted at times by the quantum transitions, we may further expect under suitable circumstances that the quantum conditions will also apply to a considerable extent to motions which are not rigorously periodic for other reasons than the interruptions produced by the sudden quantum transitions.

The application of these considerations to the above paradox is obvious. At the limit, $F=\infty$, the so-called *true* period T is only a *fictitious* period since the motion is interrupted very frequently by quantum transitions, while the so-called quasi-period θ, although not a true period, may nevertheless repeat itself many times before interruption either by a quantum transition or by the elastic reflection. Under the circumstances we expect without further uncertainty that at the limit, the quantization will be determined solely by the period θ.

In intermediate situations, where the periods T and θ are of the same order of magnitude, we seem led to the conclusion that both periods must be considered in the quantization. The a-priori probability belonging to the whole qp space will tend to concentrate at the levels allowed by both methods of quantization, and as F is made greater and greater, the quantization corresponding to the long period T will get weaker and weaker, and there will be a continuous transfer of a-priori probability from the quantum levels allowed by period T to those allowed by period θ.

It is interesting to note that in the case of the weak quantization of the radio-oscillator which we considered in the previous section, the a-priori probability lost by the quantized motions is taken up by neighboring classical motions, since all quantized motions in the given region of phase-

[2] See Bohr, Zeits. f. Physik., **13,** 152 (1923)

space are weakened. In the present case of the alternating rotator, the two types of quantized motion are in the same region of the phase-space, and the a-priori probability lost by one set of quantized motions is gained by the other set of quantized motions.

Case III (*The gallows problem*). *The true period $T=1/\omega$ is long, but the motion has a short quasi-period θ which, however, is slowly and continuously varying.*

A somewhat different model[3] will furnish an example of another class of systems. Consider the electric dipole as hung (from a gallows) on a string which gradually twists up, bringing the dipole ultimately to rest and then reversing the motion. The system thus has two periods, a long true period T, and a short quasi-period θ, which, however, varies in duration in different parts of the long period. If we use the true period T for determining the quantization we obtain permitted motions (ellipses in the phase-space) in which the angular momentum varies through the period as the string twists up, and the permitted quantum levels lie close together. If now, moreover, we make the string weaker and weaker and still quantize with respect to period T, the quantum levels come closer and closer together, and the angular momentum continues to vary in a continuous manner as the string twists up. Yet at the limit when the restoring force of the string becomes zero we know that the quantum levels must lie far apart and the angular momentum can only have the constant values $nh/2\pi$, as determined by the usual rules of quantization for rotators.

From the point of view of the present article, the paradox is again solved by the fact that quantization with respect to the true period T becomes completely washed out when T is made very long compared with the probable interval between quantum jumps. In addition we are led to the presumptive belief that as T is made longer the system tends to become quantized with respect to the quasi-period θ in spite of the fact that this quasi-period does not become truly a constant until the limit is reached. In terms of a-priori probability, quantization with respect to the variable quasi-period θ, means that the phase points tend to crowd into those regions where the angular momentum is a multiple of $h/2\pi$, and this tendency will be the greater the longer is T and the shorter and more nearly constant is θ.

Case IV (*Disturbed orbits*). *The period $T=1/\omega$ is not a true period since the motion is disturbed by accidental causes such as molecular collisions.*

By the considerations of the last two sections we have felt led to the belief that the rules of quantization must often have considerable applica-

[3] See Ehrenfest and Breit loc. cit.[1]

bility to motions which are not rigorously periodic. Even when the deviations from true periodicity are of a fortuitous nature, we shall nevertheless expect a tendency for the phase points to crowd into those regions of the phase-space which correspond to the quantization of truly periodic motions with which the actual nearly periodic motions are in approximate coincidence for a considerable length of time.

As a matter of fact the emission and absorption of definite although broadened spectral lines by molecules which are subjected to frequent collisions, as studied for example in the experiments of Füchtbauer and his associates,[4] does furnish evidence of a strong tendency to quantization, in spite of the fact that the complete periodicity of the internal motions is irregularly disturbed by the fields from neighboring molecules. The broadening of the lines may be regarded as mainly due to the changes in the energy levels of the emitting or absorbing molecule by the fields from the colliding molecules. A certain further broadening might also arise from the weakening of the quantization which presumably accompanies the disturbances in strict periodicity. This latter effect, however, may easily be negligible owing to the shortness in the period of internal motion compared with the period between collisions.[5]

Case V (The symmetrical rotator). $C_\tau = 0$ unless $\tau = i\sigma$, where i is any integer and σ is the "symmetry factor."

We desire finally to consider a very interesting and somewhat puzzling class of periodic motions, where there is no reason to expect weakened quantization due to interruption of the period by too frequent quantum transitions, but where the coefficients C_τ have such values that unit change in quantum number is excluded and the only possible transitions are those in which the quantum number changes by a multiple of a certain number σ called the symmetry factor. Under these circumstances, if we start a set of molecules all in one given quantum state and allow it to interact with thermal radiation, then at any later time it is evident the molecules will be distributed in certain quantum states but not in all quantum states, since states for which the quantum numbers differ from the original by a number which is not a multiple of σ will not have been filled. This suggests the interesting possibility that here also we may really be dealing with a case of weak quantization, so that the quota of molecules in certain quantum levels is missing because of weakened quantization.

[4] See for example, Füchtbauer, Joos and Dinkelacker, Ann. der Phys. **71**, 204 (1923)

[5] From our present point of view, the "natural" width of a spectral line from stationary isolated molecules would be due to the small "natural" weakening in quantization which accompanies the interruption in strict periodicity produced by the quantum transitions themselves.

In order to fix our attention on simple examples, we may consider rigid rotators carrying electric charges which are symmetrically placed so that rotation through the angle $2\pi/\sigma$ will return the rotator to an equivalent position. In analogy to the name dipole for the unsymmetrical rotator (HCl) formed with a positive and negative charge diametrically opposite each other, we may call the symmetrical rotators quadrupoles (H_2) [$\sigma=2$], hexapoles (CH_3Cl) [$\sigma=3$], etc. according to the submultiple of 2π necessary for the return to an equivalent position. It is evident that the Fourier analysis which would be given by the classical theory for the radiation[6] accompanying such a rotation would have the values of $C_\tau=0$ unless τ is a multiple of σ, so that quantum transitions in which the quantum number does not change by a multiple of σ will be ruled out by the correspondence principle. Thus for a quadrupole only transitions can take place in which the quantum number changes by an even number, for a hexapole the change must be a multiple of three, etc.

Let us now consider for simplicity a gas composed of quadrupoles all of which are started in the state of zero rotation, and are then subjected to the action of radiant energy, for example diatomic hydrogen started in the adsorbed or cystalline state, and then exposed to radiant energy of some definite temperature. Then it is evident from the exclusion of odd changes in quantum number, that at any later time all the quadrupoles will have values of their angular momentum which are *even* multiples of $(h/2\pi)$.[7]

This result suggests the possible conclusion that symmetrical rotators can in general only assume values of the angular momentum equal to $\sigma nh/2\pi$ and that the a-priori probability, which for unsymmetrical rotators belongs equally to all quantum levels, has for symmetrical rotators been given only to the favored levels. It also suggests the possibility

[6] In passing it should be noted that in the case of symmetrical rotators we can no longer use the Fourier analysis of the *electric moment* of the rotator as a sufficiently close approximation for determining in accordance with classical theory the amplitudes of the emitted harmonics. For a symmetrical rotator, the electric moment remains permanently zero, and the second order terms usually neglected must be considered in calculating the amplitudes of the harmonics. This means that even those values of the coefficients C_τ which do not disappear for symmetrical rotators have nevertheless extremely small values, so that the quantum transitions still allowed have a very small probability of occurrence. Hence for example, the transitions of H_2 from one rotational state to another must be very infrequent as compared with the similar transitions of HCl. Nevertheless, the known facts concerning the energy content of H_2 gas at low temperature seem to confirm our general view that the rotational states of quantization do exist and transitions from one state to another do take place.

[7] This neglects the possibility that molecules arrive in the odd quantum states by some mechanism of molecular collision.

that, accompanying a gradual change from an unsymmetrical to a symmetrical rotator, we should find a gradual weakening in the quantization of certain levels, with a transfer of a-priori probability to the remaining levels.

In the two previous cases in which we encountered the gradual transfer of a-priori probability from one set of quantum levels to another, we found that the limiting condition arrived at could itself be regarded as a new strong quantization using a different period for determining the limits of the quantum integral. This would also be true if we should accept the conclusion suggested above. If for a symmetrical rotator, we take 0 and $2\pi/\sigma$ as the limits of integration instead of 0 and 2π we should again arrive at the same conclusion that the angular momentum could only assume values equal to $\sigma nh/2\pi$, the justification for the limit $2\pi/\sigma$ being of course that at this angle the electromagnetic field conditions have identically repeated themselves, making this the limit to what we might naturally consider the period.

It should also be pointed out that the introduction of the symmetry factor in such a way as to *reduce* the number of quantum levels which can be occupied by symmetrical gaseous molecules, would apparently be in agreement with the introduction of the symmetry factor by Ehrenfest and Trkal[8] in such a way as to *reduce* the volume of the gamma-space $\{\gamma\}$ corresponding to symmetrical gaseous molecules.

At present it would seem premature to make the definite assertion that the rotation of symmetrical molecules is to be quantized using the period 0 to $2\pi/\sigma$ instead of 0 to 2π, and the possibility of such a conclusion is proposed only as a question for further discussion. It must be pointed out, nevertheless, how naturally the consideration of our five successive cases would lead to the above conclusion. In case the conclusion should be accepted, it is interesting to note that we should have now apparently found a case in which weak quantization arises from the fact that the quantum transitions in and out of a particular quantum state occur too seldom rather than too frequently.

CALIFORNIA INSTITUTE OF TECHNOLOGY
April 1924.[9]

[8] Ehrenfest and Trkal, Proc. Amsterdam Akad. **23**, 162 (1920); Ann. der Phys. **65**, 609 (1921)

[9] Received May 10, 1924—Ed.